PATENT ABSTRACTS OF JAPAN

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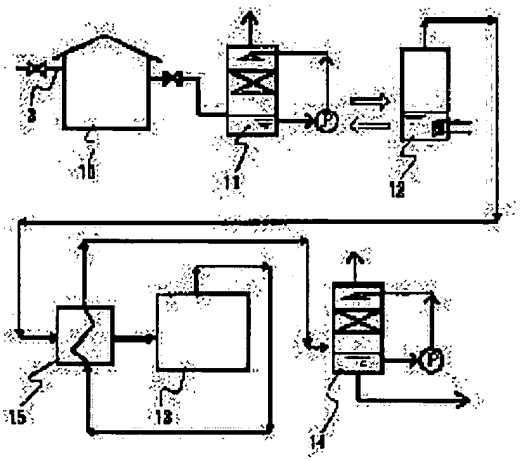
(54) TREATMENT OF METHYL BROMIDE-CONTAINING WASTE GAS

(57)Abstract:
PURPOSE: To efficiently recover methyl bromide in a waste gas contg. a minute amt. of methyl bromide used in fumigation and to easily desorb the methyl bromide.
CONSTITUTION: A methyl bromide-contg. waste gas from a fumigated warehouse 10 is brought into contact with an aq. β-cyclodextrin-soln. in an absorption tower 11 to clathrate and absorb the methyl bromide in the waste gas. The clathrated methyl bromide is desorbed from the soln. in a regeneration tank 12, and then the desorbed methyl bromide gas is burned and decomposed in a furnace 13. Consequently, the aq. soln. having clathrated and absorbed methyl bromide is easily regenerated by heating or ultrasonic irradiation and repeatedly recylced, and the discharge of methyl bromide into the atmosphere is almost completely prevented.



LEGAL STATUS

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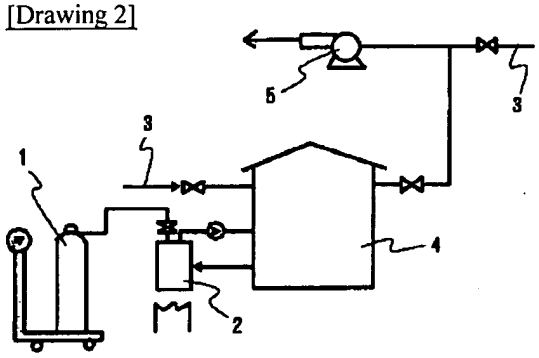
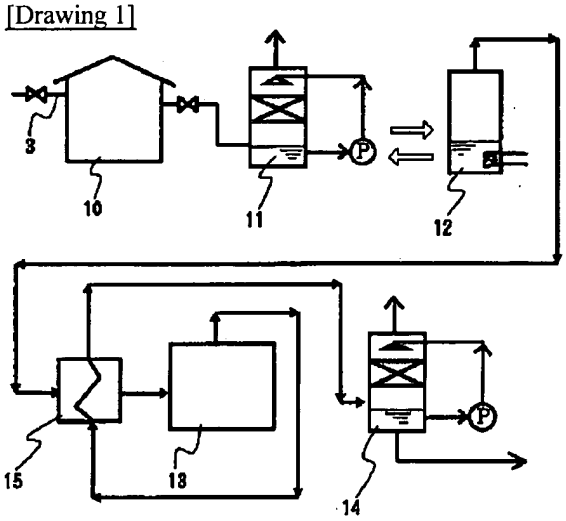
* NOTICES *

DRAWINGS

[Drawing 2]



[Drawing 1]



[Translation done.]

EXAMPLE

[Example] Next, this invention is not restricted by this example although this invention is explained to a detail based on an example with reference to a drawing.
[0010] Drawing 1 is the schematic diagram of the equipment in which one example of the approach of this invention is shown. In drawing 1 , the methyl bromide content exhaust gas in the fumigation warehouse 10 is supplied from the lower part of an absorption tower 11, and flows the inside of an absorption tower 11 by the upper counterflow. From the upper part of an absorption tower 11, the methyl bromide content exhaust gas with which beta-cyclodextrin solution is supplied to homogeneity by a spray etc., and flows by the upper counterflow is contacted, inclusion of the methyl bromide is carried out to beta-cyclodextrin, it is removed out of exhaust gas, and exhaust gas serves as sewer gas from the upper part of an absorption tower 11, and is discharged out of a system.
[0011] As for beta-cyclodextrin water solution, using as a saturated water solution is desirable. If it is desirable that it is 20-60 (a liter/hr), the speed of supply, i.e., the cavernous rate, of said exhaust gas to the capacity of beta-cyclodextrin water solution, and it is later than this, an absorption tower will become large, and if earlier than this, the rate which carries out inclusion will fall. Moreover, the range of the residence time for 2 - 8 seconds is desirable, the temperature to contact, i.e., the temperature which carries out inclusion, has desirable 5-40 degrees C, and the pressure which carries out inclusion is enough before and after ordinary pressure.
[0012] beta-cyclodextrin water solutions which carried out inclusion of the methyl bromide are collected by the pars basilaris ossis occipitalis of an absorption tower 11, they are collected in order to use it again, and they are supplied to the playback tub 12. Reuse becomes possible when beta-cyclodextrin water solution with which the capacity which carries out inclusion declined carries out desorption of the methyl bromide which carried out inclusion. Association with beta-cyclodextrin and a guest, i.e., a methyl bromide, is close to physical adsorption, and desorption is easily possible for it and it can carry out desorption of the methyl bromide easily only by warming. warming -- as for temperature, it is desirable that it is 60-70 degrees C, and, less than [this], it is not reproduced.
[0013] It is sent to the combustion cracking unit 13, and is decomposed nearly completely, and the methyl bromide which carried out desorption is converted into a hydrogen bromide, carbon dioxide gas, and a steam by the following reaction formula.
2CH3 Br+3O2 ->2 -- the temperature in the HBr+2CO2+2H2 O combustion cracking unit 13 at this time is 600-900 degrees C, carries out oxidization decomposition in this temperature requirement, and can decompose a methyl bromide 99% or more.

[0014] In addition, combustion decomposition may be carried out using the oxidation catalyst which has poisoning-proof nature in a halogenide in the combustion cracking unit 13. When an oxidation catalyst is used, 200-400-degree C low temperature is sufficient as combustion temperature, and it can use what supported manganese, copper, nickel, cobalt, platinum, palladium, etc. to the alumina, the titania, the zirconia, etc. as a catalyst.
[0015] Heat exchange of the exhaust gas decomposed with the combustion cracking unit 13 is carried out to the exhaust gas which contains a methyl bromide by the heat exchanger 15, after cooling in temperature of 50 degrees C or less with the condensator further omitted to drawing 1 , a sodium-hydroxide solution is made to absorb the hydrogen bromide which is cracked gas in an absorption tower 14, it collects as a harmless sodium bromide, and the gas after absorption is emitted into atmospheric air. The alkali solution discharged from the pars basilaris ossis occipitalis of an absorption tower 14 is neutralized and defanged with a hydrochloric acid etc.
[0016] In the above-mentioned example, although desorption of the methyl bromide from beta-cyclodextrin was performed by warming at 60-70 degrees C, a supersonic wave is irradiated with a sink and it can also carry out desorption of the inert gas, such as nitrogen gas. Moreover, although combustion decomposition of the methyl bromide which carried out desorption was carried out, it is also reusable to fumigation.

[Translation done.]

PRIOR ART

[Description of the Prior Art] Conventionally, the methyl bromide is used for fumigation processing of brown rice and wheat, and as shown in drawing 2 , after the methyl bromide in the methyl bromide bomb 1 is made into methyl bromide gas with evaporation equipment 2, it is sent to the fumigation warehouse 4. After fumigation processing is completed, a lot of diluting airs are made to mix in fumigation equipment 4 compulsorily from dilution sky air conduction ON tubing 3, methyl bromide gas is diluted, the methyl bromide concentration in exhaust gas is lowered, and it is emitting into atmospheric air using the exhaust gas blower 5. However, by this approach, since it does not mean reducing the total amount of a methyl bromide, it cannot be said to be fundamental prevention of pollution. Moreover, since the methyl bromide is made into the causative agent of ozone layer depletion like chlorofluocarbon, development of the technique of reducing the burst size to atmospheric air is desired strongly.

[0003] An activated-charcoal-absorption method can be considered as an approach of carrying out recovery removal of the methyl bromide in exhaust gas. In recent years, a device is given to the ingredient of activated carbon, the desorption approach, reconstructive processing, etc., and recovery effectiveness is rising. activated carbon -- the grain from a configuration -- it is divided spherically and fibrous, granular and fibrous activated carbon is used for fixed-bed-type equipment, and spherical activated carbon is used for the equipment of a fluidized bed.

[0004] The desorption approach of the matter which stuck to activated carbon has the temperature swinging method and the pressure swinging method, and the approach that combined these further. The difference of the amount of adsorption by the temperature of an adsorbent is used for the temperature swinging method, and a steam or gas is used. Although steam desorption is used for fixed-bed-type equipment, it has the problem that the waste water treatment of the water of condensation is needed, or adsorption capacity falls with the moisture which remained in activated carbon. Although gas desorption is used for the equipment of a fluidized bed, it has a possibility that fluctuation of airflow may be large and may cause damage on activated carbon. On the other hand, it is said that power expense attaches the pressure swinging method to a high thing for pressure operated although the difference of the amount of adsorption by the pressure is used and gas desorption is adopted. It is anxious for development of a pollution-free-ized art with the sufficient effectiveness of the methyl bromide content exhaust gas replaced with an activated-charcoal-absorption method to the bottom of such a situation.

[Translation done.]

* NOTICES *

1.This document has been translated by computer. So the translation may not reflect the original precisely.
2.**** shows the word which can not be translated.
3.In the drawings, any words are not translated.

DESCRIPTION OF DRAWINGS

[Brief Description of the Drawings]
[Drawing 1] It is the schematic diagram of the equipment in which one example of this invention is shown.
[Drawing 2] It is the schematic diagram showing the art of conventional fumigation methyl bromide exhaust gas.
[Description of Notations]
1 Methyl Bromide Bomb
2 Evaporation Equipment
3 Dilution Airstream ON Tubing
4 Fumigation Warehouse
5 Exhaust Gas Blower
10 Fumigation Warehouse
11 Absorption Tower
12 Playback Tub
13 Combustion Cracking Unit
14 Absorption Tower
15 Heat Exchanger

[Translation done.]

DETAILED DESCRIPTION

[Detailed Description of the Invention]
[0001]
[Industrial Application] or [understanding a methyl bromide a burned part, while this invention relates to the art of the exhaust gas containing the methyl bromide used for fumigation and removing and defanging a methyl bromide from exhaust gas in more detail] -- or it is related with the art whose reuse is enabled.
[0002]
[Description of the Prior Art] Conventionally, the methyl bromide is used for fumigation processing of brown rice and wheat, and as shown in drawing 2 , after the methyl bromide in the methyl bromide bomb 1 is made into methyl bromide gas with evaporation equipment 2, it is sent to the fumigation warehouse 4. After fumigation processing is completed, a lot of diluting airs are made to mix in fumigation equipment 4 compulsorily from dilution sky air conduction ON tubing 3, methyl bromide gas is diluted, the methyl bromide concentration in exhaust gas is lowered, and it is emitting into atmospheric air using the exhaust gas blower 5. However, by this approach, since it does not mean reducing the total amount of a methyl bromide, it cannot be said to be fundamental prevention of pollution. Moreover, since the methyl bromide is made into the causative agent of ozone layer depletion like chlorofluocarbon, development of the technique of reducing the burst size to atmospheric air is desired strongly.
[0003] An activated-charcoal-absorption method can be considered as an approach of carrying out recovery removal of the methyl bromide in exhaust gas. In recent years, a device is given to the ingredient of activated carbon, the desorption approach, reconstructive processing, etc., and recovery effectiveness is rising. activated carbon -- the grain from a configuration -- it is divided spherically and fibrous, granular and fibrous activated carbon is used for fixed-bed-type equipment, and spherical activated carbon is used for the equipment of a fluidized bed.
[0004] The desorption approach of the matter which stuck to activated carbon has the temperature swinging method and the pressure swinging method, and the approach that combined these further. The difference of the amount of adsorption by the temperature of an adsorbent is used for the temperature swinging method, and a steam or gas is used. Although steam desorption is used for fixed-bed-type equipment, it has the problem that the waste water treatment of the water of condensation is needed, or adsorption capacity falls with the moisture which remained in activated carbon. Although gas desorption is used for the equipment of a fluidized bed, it has a possibility that fluctuation of airflow may be large and may cause damage on activated carbon. On the other hand, it is said that power expense attaches the pressure swinging method to a high thing for pressure operated although the difference of the amount of adsorption by the pressure is used and gas desorption is adopted. It is anxious for development of a pollution-free-ized art with the sufficient effectiveness of the methyl bromide content exhaust gas replaced with an activated-charcoal-absorption method to the bottom of such a situation.
[0005]
[Problem(s) to be Solved by the Invention] This invention cancels the fault of said conventional technique, it collects efficiently the methyl bromides in the exhaust gas containing the methyl bromide of the minute amount used for fumigation, can carry out desorption easily, and aims at offering the approach whose reuse is enabled.
[0006]
[Means for Solving the Problem] This invention is completed based on knowledge that beta-cyclodextrin contacts a methyl bromide and forms a clathrate compound. It condenses and the methyl bromide used for fumigation processes, in order to understand a removed part economically from being discharged as rare gas. This invention uses generation of a clathrate compound for this concentration process.
[0007] That is, after the art of the methyl bromide content exhaust gas by this invention carries out desorption of the methyl bromide which the methyl bromide content exhaust gas used for fumigation was contacted in beta-cyclodextrin water solution, carried out inclusion absorption of the methyl bromide in exhaust gas, and carried out inclusion of this beta-cyclodextrin water solution, it is characterized by understanding the methyl bromide gas which carried out desorption a burned part, or reusing to fumigation.
[0008] beta-cyclodextrin used for this invention is annular grape sugar which hydrolyze starch by the amylase and are obtained. Generally, since many hydroxyl groups have come out of cyclodextrin to the outside of a ring, the inside is hydrophobicity to an outside being a hydrophilic property. And since a methyl bromide is incorporated by this inside and a clathrate compound is formed, recovery removal of the methyl bromide of the minute amount used for fumigation can be carried out from exhaust gas. In this clathrate compound, association with beta-cyclodextrin is close to physical adsorption,

desorption is easily possible for the methyl bromide by which inclusion was carried out, by warming at 60-70 degrees C, desorption can be carried out or desorption of the inert gas can be carried out by irradiating a supersonic wave with a sink. Therefore, beta-cyclodextrin can be repeated and used. Moreover, the methyl bromide which carried out desorption may be reused to fumigation, and may carry out combustion decomposition.
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[0017]
[Effect of the Invention] or [reusing to fumigation the methyl bromide which became possible / carrying out absorption inclusion of the methyl bromide to beta-cyclodextrin, and condensing it by contacting the exhaust gas which contains extremely the methyl bromide used for fumigation by low concentration in beta-cyclodextrin solution according to the approach of this invention, /, and could repeat and reuse beta-cyclodextrin since desorption was easy, and carried out desorption] -- or combustion decomposition can carry out and it can defang. Furthermore, this approach can reduce operation cost sharply as compared with the conventional activated-charcoal-absorption method.

[Translation done.]

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	53/77				
	53/34	ＺＡＢ			
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				ＺＡＢ	

審査請求　未請求　請求項の数１　ＦＤ　（全４頁）

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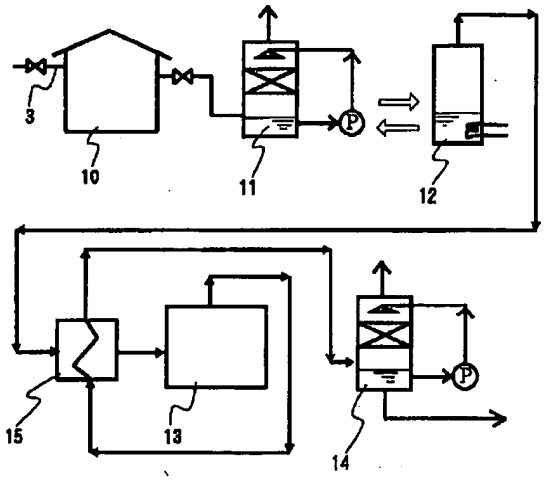
(54)【発明の名称】　臭化メチル含有排ガスの処理方法

(57)【要約】

【目的】　くん蒸に用いた微量の臭化メチルを含む排ガス中の臭化メチルを効率よく回収し、容易に脱着できる方法を提供すること。

【構成】　くん蒸倉庫１０からの臭化メチル含有排ガスを吸収塔１１内でβ－シクロデキストリン水溶液と接触させて排ガス中の臭化メチルを包接吸収し、このβ－シクロデキストリン水溶液を再生槽１２内で包接した臭化メチルを脱着させた後、脱着した臭化メチルガスを燃焼分解炉１３内で燃焼分解することを特徴とする臭化メチル含有排ガスの処理方法である。

【効果】　臭化メチルを包接吸収したβ－シクロデキストリン水溶液は、加温又は超音波照射により容易に脱着でき、繰り返し再利用することができ、大気中への臭化メチルの放出をほとんど完全に防止することができる。



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【特許請求の範囲】

【請求項1】　くん蒸に用いられた臭化メチル含有排ガスをβ－シクロデキストリン水溶液と接触させて排ガス中の臭化メチルを包接吸収し、このβ－シクロデキストリン水溶液から包接した臭化メチルを脱着させた後、脱着した臭化メチルガスを燃焼分解するか又はくん蒸に再利用することを特徴とする臭化メチル含有排ガスの処理方法。

【発明の詳細な説明】

【０００１】

【産業上の利用分野】本発明は、くん蒸に用いられた臭化メチルを含有する排ガスの処理方法に係り、さらに詳しくは、排ガスから臭化メチルを除去、無害化すると共に、臭化メチルは燃焼分解するか又は再利用可能にする処理方法に関する。

【０００２】

【従来の技術】従来、玄米や小麦のくん蒸処理には、臭化メチルが使用されており、図２に示すように、臭化メチルボンベ１内の臭化メチルは、気化装置２で臭化メチルガスとされた後、くん蒸倉庫４へ送られる。くん蒸処理が完了した後には、希釈空気導入管３から大量の希釈空気を強制的にくん蒸装置４内に混入させて臭化メチルガスを希釈し、排ガス中の臭化メチル濃度を下げて排ガスブロワ５を用いて大気中に放出している。しかしながら、この方法では臭化メチルの総量を低減したことにならないため、基本的な公害防止とは言えない。また、臭化メチルは、フロンと同様にオゾン層破壊の原因物質とされているため、大気への放出量を低減する技術の開発が強く望まれている。

【０００３】排ガス中の臭化メチルを回収除去する方法としては、活性炭吸着法が考えられる。近年、活性炭の材料、脱着方法、再生プロセス等に工夫が施され、回収効率が上昇している。活性炭は、形状からは粒状、球状及び繊維状に分けられ、粒状及び繊維状の活性炭は固定床式の装置に用いられ、球状活性炭は、流動床式の装置に用いられる。

【０００４】活性炭に吸着した物質の脱着方法は、温度スイング法及び圧力スイング法、さらにはこれらを組み合わせた方法がある。温度スイング法は、吸着剤の温度による吸着量の差を利用するもので、水蒸気又はガスが用いられる。水蒸気脱着は、固定床式の装置に用いられるが、凝縮水の廃水処理が必要となったり、活性炭内に残った水分によって吸着能が低下するという問題がある。ガス脱着は、流動床式の装置に使用されるが、風量の変動が大きく、また、活性炭の損傷を招く恐れがある。他方、圧力スイング法は、圧力による吸着量の差を利用するもので、ガス脱着が採用されているが、圧力操作のため動力費が高いものにつくと言われている。このような状況の下に、活性炭吸着法に代わる臭化メチル含有排ガスの効率のよい無公害化処理方法の開発が切望されている。

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【０００５】

【発明が解決しようとする課題】本発明は、前記従来技術の欠点を解消し、くん蒸に用いた微量の臭化メチルを含む排ガス中の臭化メチルを効率よく回収し、容易に脱着でき、再利用可能にする方法を提供することを目的とする。

【０００６】

【課題を解決するための手段】本発明は、β－シクロデキストリンが臭化メチルと接触して包接化合物を形成するとの知見に基づいて完成したものである。くん蒸に用いた臭化メチルは、希ガスとして排出されることから経済的に除去分解するには、濃縮して処理する。本発明は、この濃縮工程に包接化合物の生成を利用したものである。

【０００７】すなわち、本発明による臭化メチル含有排ガスの処理方法は、くん蒸に用いられた臭化メチル含有排ガスをβ－シクロデキストリン水溶液と接触させて排ガス中の臭化メチルを包接吸収し、このβ－シクロデキストリン水溶液を包接した臭化メチルを脱着させた後、脱着した臭化メチルガスを燃焼分解するか又はくん蒸に再利用することを特徴とする。

【０００８】本発明に用いるβ－シクロデキストリンは、でんぷんをアミラーゼで加水分解して得られる環状ブドウ糖である。一般に、シクロデキストリンは、環の外側に水酸基が多数でているので、外側は親水性であるのに対して、内側は疎水性である。そして、この内側に臭化メチルが取り込まれて包接化合物を形成するので、くん蒸に用いた微量の臭化メチルを排ガスから回収除去することができる。この包接化合物において、β－シクロデキストリンとの結合は、物理吸着に近いもので、包接された臭化メチルは容易に脱着可能であり、６０～７０℃に加温することにより脱着するか、又は不活性ガスを流しながら超音波を照射することによって脱着することができる。したがって、β－シクロデキストリンを繰り返し使用することができる。また、脱着した臭化メチルは、くん蒸に再利用してもよいし、燃焼分解してもよい。

【０００９】

【発明の実施例】次に、図面を参照して本発明を実施例に基づいて詳細に説明するが、本発明はこの実施例によって制限されるものではない。

【００１０】図１は、本発明の方法の一実施例を示す装置の系統図である。図１において、くん蒸倉庫１０内の臭化メチル含有排ガスは、吸収塔１１の下部から供給され、吸収塔１１内を上向流で流れる。吸収塔１１の上部からは、β－シクロデキストリン溶液がスプレー等で均一に供給され、上向流で流れてくる臭化メチル含有排ガスと接触し、臭化メチルはβ－シクロデキストリンに包接されて排ガス中から除去され、排ガスは吸収塔１１の

上部から浄化ガスとなって系外に排出される。

【００１１】β－シクロデキストリン水溶液は、飽和水溶液として用いるのが好ましい。β－シクロデキストリン水溶液の容量に対する前記排ガスの供給速度、すなわち、空洞速度は２０～６０（リットル／ｈｒ）であるのが好ましく、これより遅ければ吸収塔が大きくなり、これより早いと包接する割合が低下する。また、滞留時間は２～８秒の範囲が好ましく、接触させる温度、すなわち、包接させる温度は５～４０℃が好ましく、包接させる圧力は常圧前後で充分である。

【００１２】臭化メチルを包接したβ－シクロデキストリン水溶液は、吸収塔１１の底部に収集され、再度使用するために回収して再生槽１２に供給される。包接する能力が低下したβ－シクロデキストリン水溶液は、包接した臭化メチルを脱着することによって再生利用が可能になる。β－シクロデキストリンとゲスト、すなわち、臭化メチルとの結合は、物理吸着に近いもので、臭化メチルを容易に脱着可能であり、加温のみで容易に脱着することができる。加温温度は６０～７０℃であるのが好ましく、これ以下では再生されない。

【００１３】脱着した臭化メチルは、燃焼分解炉１３に送られ、ほぼ完全に分解され、下記の反応式により臭化水素、炭酸ガス及び水蒸気に転換される。

$2CH_3Br+3O_2 \rightarrow 2HBr+2CO_2+2H_2O$

このときの燃焼分解炉１３内の温度は６００～９００℃であり、この温度範囲で酸化分解して、臭化メチルを９９％以上分解できる。

【００１４】なお、燃焼分解炉１３にハロゲン化物に耐被毒性を有する酸化触媒を用いて燃焼分解してもよい。酸化触媒を用いた場合、燃焼温度は２００～４００℃の低温でもよく、触媒としてはアルミナ、チタニア、ジルコニア等にマンガン、銅、ニッケル、コバルト、白金、パラジウムなどを担持したものを使用することができる。

【００１５】燃焼分解炉１３で分解された排ガスは、熱交換器１５で臭化メチルを含む排ガスと熱交換され、さらに図１に省略した冷却器で温度５０℃以下に冷却した後、吸収塔１４で水酸化ナトリウム溶液に分解ガスである臭化水素を吸収させて無害の臭化ナトリウムとして回収し、吸収後のガスは大気中に放出される。吸収塔１４の底部から排出されるアルカリ溶液は、塩酸などで中和して無害化される。

【００１６】上記実施例においては、β－シクロデキストリンからの臭化メチルの脱着は、６０～７０℃に加温することにより行ったが、窒素ガスなどの不活性ガスを流しながら超音波を照射して脱着することもできる。また、脱着した臭化メチルを燃焼分解したが、くん蒸に再利用することもできる。

【００１７】

【発明の効果】本発明の方法によれば、くん蒸に用いた臭化メチルを極めて低濃度で含む排ガスをβ－シクロデキストリン溶液と接触させることによって臭化メチルをβ－シクロデキストリンに吸収包接させて濃縮することが可能となり、また、脱着が容易であるため、β－シクロデキストリンを繰り返し再利用することができ、脱着した臭化メチルはくん蒸に再利用するか又は燃焼分解して無害化することができる。さらに、この方法は、従来の活性炭吸着法に比較して運転コストを大幅に低減することができる。

【図面の簡単な説明】

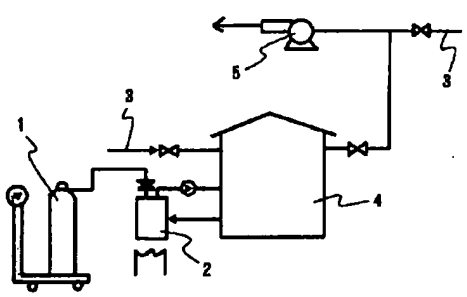
【図１】本発明の一実施例を示す装置の系統図である。

【図２】従来のくん蒸臭化メチル排ガスの処理方法を示す系統図である。

【符号の説明】

１　臭化メチルボンベ
２　気化装置
３　希釈空気流入管
４　くん蒸倉庫
５　排ガスブロワ
１０　くん蒸倉庫
１１　吸収塔
１２　再生槽
１３　燃焼分解炉
１４　吸収塔
１５　熱交換器

【図２】



【図1】